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Nanoremediation

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ABSTRACT:
Pollution of soils is becoming a major problem in the world and especially, for most of the developed countries of the world. The crops cultivated in polluted soils may be containing a high level of heavy metals and/or toxic materials that can effect on human health. So, it is necessary to use the different technologies to clean up the polluted soil and creates additional lands for agricultural uses.
Nanotechnology offers a wide number of smarter and cheaper techniques can be used as alternative methods to immobilize contaminants such as; nanoremediation technology. The nanoremediation methods entail the nanomaterials application on polluted soil. Additionally, this method has the potential to reduce the high costs of soil remediation for large-scale and the time of cleanup. Also, may be reducing toxic materials concentration or heavy metals to near zero in situ. This review aims to of nanotechnology application on contaminated soil remediation.
Key Words: Heavy Metals, Environmental Pollution, Nanoparticles, Nanoremediation

INTRODUCTION:
Nanotechnology is an advanced modern technique and alternative for traditional remediation methods (ex-situ and in-situ technologies). It provides new kinds of materials (nanomaterials) have properties that enable both chemical reduction and catalysis to transformation and detoxification of pollutants. Nanoremediation methods entail the nanomaterials application on polluted soil.

NANOMATERIALS:
Nanomaterials (NMs) are materials have nanoscaled dimensions of 100 nm or less in at least one dimension, these materials have highly desired and required properties for soil contamination remediation and nanoparticles are those that have at least two dimensions between 1 and 100 nm. Due to the specific properties of nanomaterials such as larger specific surface area, structure and smaller particle size, they allow significantly changed the physical, chemical, biological properties and adsorption /or reactions effects on the nanoscale with the surrounding contamination media (soil). The characteristic of nanomaterials makes its more reactive than those materials used in traditional remediation technologies for soil remediation [1]. Also, they many different materials in nanoscale can be using for soil remediation such as metal oxides, titanium dioxide, carbon nanotubes, and zeolites in nanoscale. Nanomaterials can be produced by different ways of technologies, and they were classified into two mainly groups: (1) the group of technology is from outside to inside (top down), in generally turning the bigger bulk material into smaller. (2) The group of technology is a bottom to top (bottom-up), in this group, small materials will build bigger bulk material[2]. In recent years, the uses of nanotechnology application for polluted soil remediation have been significant increased. The NMs can be classified according to their properties (physical/chemical) into groups: The first group is organic nanomaterials, where mostly content carbon atoms. The second is inorganic nanomaterials and can be classified into subgroups such as (i) metal (Au-Ag) (ii) metal oxide (ZnO2-Fe2O3) (iii) quantum dots (Cd-Se). Figure (1) shows the classification of the NMs according to their physicochemical properties [3].

NANOPARTICLES PHYSICAL AND CHEMICAL PROPERTIES:
The NPs have specific properties such as specific surface area, particle size distribution,

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and morphological sub-structure of the substance, surface charge, and crystallographic characterization. These properties enhanced nanoparticle to be the key of remediation. Additionally, the natural NPs in soil include clays, organic matter, iron oxides, and other minerals are an important fraction in biogeochemical processes.

NONMATERIAL'S FOR SOIL REMEDIATION :

Pollution in the soil can be cleaned up (remediation) using a range of techniques. Nanotechnology is an advanced modern technique used in remediation of polluted soil. Recently, nanoremediation is considered a new technology and is still in progress.

Nanoremediation methods are involves removing contamination from the soil by using nanomaterials as new techniques. Nanomaterials have specific properties and can be applied in different ways in soil remediation. The using of nanoremediation methods have advantages compared with traditional remediation technologies, that is may be due to smaller particle size and specific surface area of nanomaterial and easy to moving into the soil porous. Also, for these reasons can be used for in situ application. In addition, this method is more practice and economic for remediation because it does not travel very far from the target point[4] Many different nonmaterials have been suggested for soil remediation such as nano scale zeolites, metal oxides, carbon nanotubes and fibers, titanium dioxide, zero-valent iron, iron oxides nanoparticles.
Also, nanoscale zero-valent iron (nZVI) is recently more used for polluted soil remediation. Tables (1) show some examples of nanoparticles materials application in the cleanup of contaminated soil [5].

NANOSCALE ZERO-VALENT IRON PARTICLES (NZVI):

Nanoscale Zero-Valent Iron Particles (nZVI) are one of the most common types of nanoremediation techniques and they range from 10 to 100 nm in diameter. Generally, the nZVI can be distribution and mobility once injected into a soil to remediation of contamination by moving of nanoscale material in the soil pores[4]. Because of their properties such as high available surface area, high reaction, and high efficiency can be used in in- situ remediation technology [6] .

MECHANISM OF NZVI METHODS IN DECONTAMINATION:

Nanoremediation technologies based on using NPs for remediation can be divided into two groups depending on their chemical reaction: the first group is used NPs as an electron donor to clean up the contamination in a low level of toxic with slow moving in the media (soil), and the second group the NPs using as an agent of sorbent and it is more stable for toxic fixation, also, can be using the NPs as precipitant or coprecipitant of the contaminated materials. In particular, NPs have a high absorption ratio for metal, arsenic (As), chromium (Cr), lead (Pb), mercury (Hg), selenium (Se), copper (Cu), uranium (U) (anionic contaminants), natural organic matter, organic acids, and heavy metals[5]. The reaction between toxic materials and the NPs by using the zNIP technique depending on higher surface area of these materials and by simply of that this material can be sequestration of contaminated or toxic material by two ways firstly by encapsulation of toxic materials in interface of NP aggregates, and secondly by fixation on complexation surface[5]. In general, the chemical reaction processing in zero-valent iron (Fe0) nanoparticles for removes the halogenated organic contaminants and heavy metals form soil can be expelling by following equations:

$Fe0 \rightarrow Fe2+ + 2e-$ -------------------------------- (Eqn.1)

$Fe0 \rightarrow Fe3+ + 3e-$ -------------------------------- (Eqn 2)

$RCl + H+ + 2e- \rightarrow RH + Cl-$------------------- (Eqn 3)

$RCl + Fe0 + H+ \rightarrow RH + Fe2+ + Cl-$---------- (Eqn 4)

As showing in the above reaction the metallic iron (Fe0) using as an electron donor (first

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way of clean up), and very fast transformed into Fe^{2+} (Eq.1), also, may be gradually by more time to Fe^{3+} (Eq.2). While in (Eq.3) using the reduction reaction between chlorinated hydrocarbons and the electrons for dechlorination of soil. On the other hand by thermodynamic processes may be acceptable the coupling of the reactions (Eq.1) and (Eq.3) as showed in (Eq4). The chemical mechanisms of nano-zerovalent iron (Fe0) is as shown in (Figure 2)

In generally, the standard reduction potential (E◦) of metallic iron (Fe0) to transfer to the (Fe^{2+}/Fe) during the reaction by dissolved in water is (- 0.44 mV), indicating that the high capacity of metallic iron (Fe0) to reducing contamination of many organic compounds such as chlorinated hydrocarbons and metals (Pb, Cd, Ni, Cr). The degradation of organic contaminants by zero-valent iron (Fe0) methods has two common processes[7] : (i) the first process is hydrogenolysis, where in chlorinated compounds the chlorine atom is replacement by hydrogen atom as presented in equation (Eq.5), and (ii) the second process is dehalogenation, where no addition of hydrogen, but a new C—C bond can be formed and depending on carbon connected can be divided to β reaction (connected with neighbor carbon), and the α reaction may be connected with same carbon. These reactions are presented in (Eq.6) and (Eq.7), respectively[8,9]

$ClHC{=}CCl_2 + 2e^- + H^+ \rightarrow ClHC{=}ClHC + Cl^-$ ------------ (Eqn 5)

Reaction β: $ClHC{=}CCl_2 + 2e^- \rightarrow HC{\equiv}CCl + 2Cl^-$--------- (Eqn 6)

Reaction α: $Cl_2C{=}CH_2 + 2e^- \rightarrow H_2C{=}C{:} + 2Cl^-$---------- (Eqn 7)

In soil remediation by zero-valent iron (Fe0) methods is better using the dehalogenation reaction than hydrogenolysis process that is because may be formation a new product more injurious than the contaminant source as result of hydrogenolysis reactions [7,10]. Thus Nanotechnology provides the possibility of producing the product (nanomaterials) of high quality and low cost for soil remediation compared with old methods. Nanoremediation technologies entail the application of nanomaterials for absorption, detoxification, and release of pollutants from the soil in situ remediation technique. Also, the nZVI methods can be using for the destruction of chlorinated hydrocarbons in soil.

DRAWBACKS & RISKS OF NANOPARTICLES:

The use of nanoparticles is a rapidly emerging technique with large number of benefits. Studies show it to be a very quick and efficient method for remediation of ground water and surface water[11]as well as the contaminated soil[12].There still exists certain drawbacks and risks associated with the use of nanoparticles such as

1.Nano zero valent iron (nZVI), which may be attributed to the lack of proper or complete knowledge on the way these nanoparticles behave in the environment and their possible ecological implications.

2.High concentrations of nZVI can agglomerate to form clusters, thus losing the effectiveness as a nanoparticle.

3.Further, the risk to human and ecological health still remains unknown[13]. Nanoparticles because of their small size and higher mobility can easily disperse in the environment and thus spread to larger distance causing ecotoxicity. The nanoparticles are also highly persistent in nature and have the risk of bio-accumulating in the living organisms[14].

4. Certain nanoparticles like nZVI have wide adverse effect on living entities. Certain bacterial pure cultures like the sulphate reducing bacteria are able to oxidize nZVI. However, oxidization of high concentration of nZVI leads to the formation of reactive oxygen species (ROS)[15]. Generation of ROS may cause oxidative stress, damaging the cell membrane and may ultimately lead to death.

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5.Reports suggest that higher concentration of nZVI in plants show stronger toxic effect, thus reducing the transpiration rate and translocation to the shoots[16]. Reduced transpiration and translocation in the plants may result in stunted growth of some plants and may lead to death of the plant after an exposure for an extended period. In case of humans, exposure of nanoparticles has been reported to cause genotoxicity, inflammation oxidative stress, lipid peroxidation, pulmonary disease[17] and may ultimately lead to death.

SOLUTIONS TO DRAW BACK OF NANOREMEDIATION:

The technique of nanoremediation although being very quick and efficient has numerous drawbacks and ecological risks associated as discussed in the previous section. The problems related, can be sorted out by providing better solutions for effective management of the same.

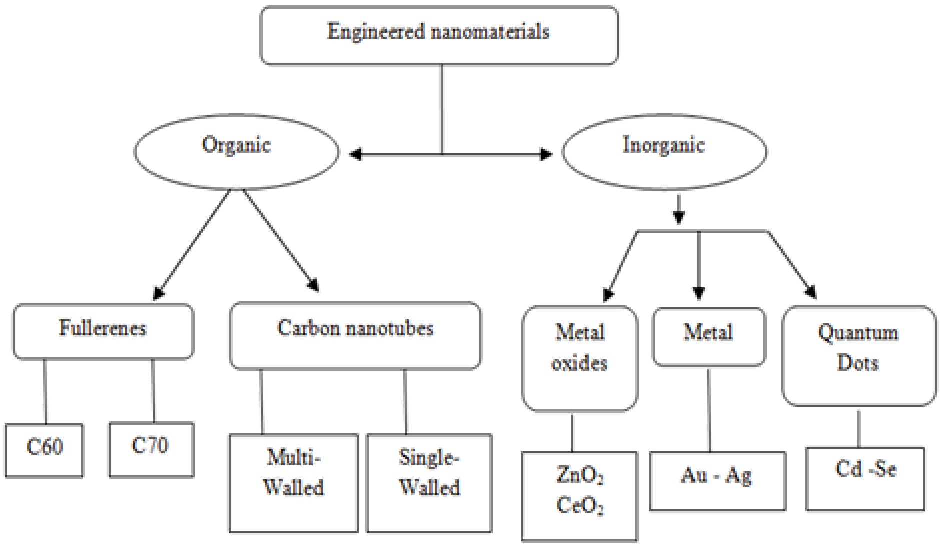

Fig. 1. Nanomaterial classification according to their physical—chemical properties

Table 1.Some contaminated materials have been treated with Nanoparticle

Classification of materials	**Example for contaminated materials**
Organics Chlorinated solvents	Organophosphorusp-chlorophenol-Antibiotcs-Pesticidasclorados
Inorganics anions	Nitrate-perchlorate- bromated
Metals Chrome	Chrome - cobalt- lead-copper- molybdenum-nickelsilver-zinc- technetium; vanadium- cadmium

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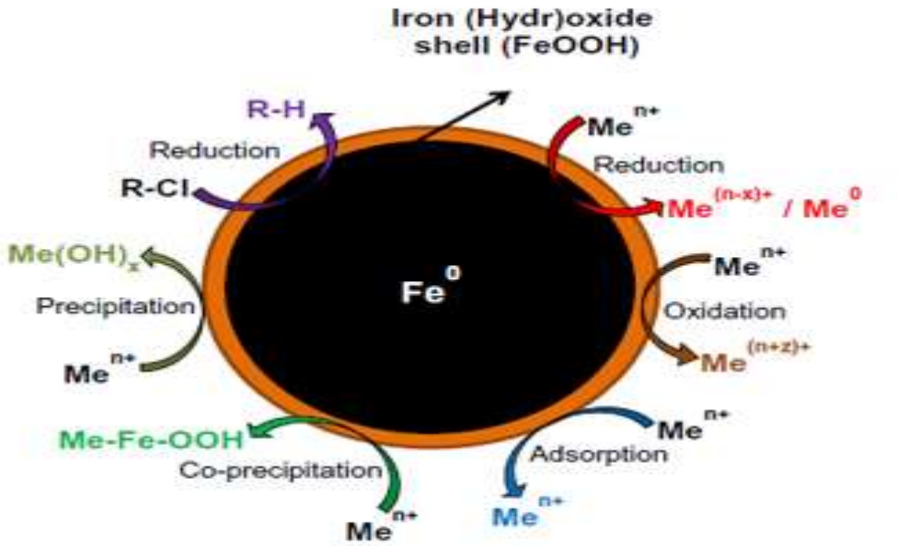

Fig.2. The chemical mechanisms of Nano-zerovalent iron (fe0)

1.Use of green nanoparticles synthesized from plant and plant parts[18] reduces release of toxic by-products into the environment[19], thus reducing ecological toxicity.

2.Similarly, employing nanoparticles derived from microbes also known as bio-nanoparticles can be a quick and efficient method for biodegradation of heavy metals present in acid mine water. Fungi also referred to as 'Nanofactories' are extremely suitable for synthesising metal nanoparticles[20].

3.The drawbacks related to zero valent iron can be overcome by use of emulsified zero valent iron (E-ZVI) which are prepared by encapsulating iron nano particles in biodegradable oil membrane. This is because the surface coating protects the zero valent iron nano particle from other constituents or inorganic pollutants, which may react with the iron, reducing its capacity[21].

As a solution to the problems the activity of plants before selection for the remediation process must be well studied and its effectiveness should be confirmed. Use of ideal plants along with suitable soil amendments and rhizospheric microorganisms, all together as a system can prove to be an effective remedial strategy. Consumption of the plants involved in the remediation process can be prevented by fencing the area earmarked for phytoremediation.

CONCLUSION :

Recently, the world facing a rapid increase in population with decreasing of food production and agricultural soils, due to soil pollution by humans activities and we need to provide additional land for agricultural uses by adopting a new and advanced technique for the soil remediation. Nanotechnology provides the possibility of producing the product (nanomaterials) of high quality and low cost for soil remediation compared with old methods. Nanoremediation technologies entail the application of nanomaterials for absorption, detoxification, and release of pollutants from the soil in situ remediation technique. Also, the nZVI methods can be using for the destruction of chlorinated hydrocarbons in soil.

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